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Preliminary communication

The molecular structure of two methylallylnorbornyl complexes of nickel(II)

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SUMMARY

The structures of two isomeric Ni^{II} complexes with different molecular configurations have been determined by X-ray diffraction studies.

In a previous communication[1] we reported the molecular structure of di-μ-acetatobis(2-methylallyl-3-norbornyl)dipalladium(II) (Complex I), one of the complexes prepared by Gallazzi *et al.*[2] with the aim of clarifying the mechanism of the insertion of norbornene into various metal–allyl bonds. In their paper Gallazzi *et al.* reported also the preparation of a nickel complex (Complex II) which appeared to be structurally identical to I. However it was soon realized that by changing only slightly the experimental conditions, it was possible to obtain crystals of another nickel complex (Complex III) with the same formula $(C_{11}H_{17}Ni{-}O{-}CO{-}CH_3)_2$ as II, but with a different crystal and molecular structure.

We have now determined the structure of both nickel complexes by X-ray diffraction methods, using an automated four-circle diffractometer for measuring the intensities of the Bragg reflections.

The crystal data are as follows: II: $a = 11.733(2)$, $b = 12.464(2)$, $c = 17.358(3)$ Å; space group *Pbcn*; 4 dimeric molecules per unit cell; 3707 measured reflections (2039 observed). III: $a = 16.131(3)$, $b = 9.846(2)$, $c = 16.007(3)$ Å, $\beta = 91°18'(2)$; space group $P2_1/c$; 4 dimeric molecules per unit cell; 3646 measured reflections (2416 observed).

Mo-K_α radiation and small crystals of regular shapes were used in both cases. Refinement of the structure of III is still in progress. For II the final value of the conventional R factor is 0.045 on the basis of the observed reflections only; for III the value of R has been calculated as 0.073.

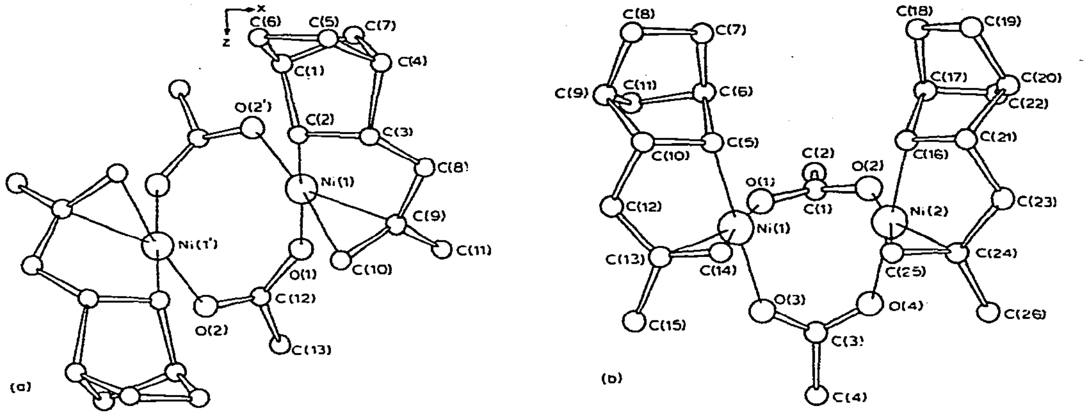

Fig. 1. (a) II: a projection of the dimeric molecule in the x–z plane; (b) III: a projection of the dimeric molecule in a plane containing the two Ni atoms.

In both cases the coordination about each Ni ion is approximately square planar but, while II (Fig. 1a) is in fact isostructural with I with its molecular symmetry axis coincident with one of the crystallographic twofold axes parallel to b, III has the molecular structure presented in Fig. 1b with an approximate mirror plane passing through the carbon atoms C(2), C(1), C(3), and C(4) of the bridging acetate groups. These different molecular configurations together with the *trans* effect exerted by the σ-bonded carbon atoms of the norbornyl moieties onto the Ni–O distances (see Table 1) have the consequence that while in II (and also in I) the oxygen atoms of the two bridging groups form equivalent bonds with the metal ions, in III one of the two acetate groups is more

TABLE 1

BOND DISTANCES (Å) AND ANGLES (°)

Complex II		*Complex III*	
Ni(1)–Ni(1')	2.984(1)	Ni(1)–Ni(2)	3.064(2)
Ni(1)–O(1)	1.996(4)	Ni(1)–O(3)	1.962(8)
		Ni(2)–O(4)	1.997(8)
Ni(1)–O(2')	1.912(3)	Ni(1)–O(1)	1.890(7)
		Ni(2)–O(2)	1.893(8)
Ni(1)–C(2)	1.955(5)	Ni(1)–C(5)	1.967(10)
		Ni(2)–C(16)	1.965(10)
Ni(1)–C(9)	2.069(5)	Ni(1)–C(13)	2.063(11)
		Ni(2)–C(24)	2.079(11)
Ni(1)–C(10)	2.020(6)	Ni(1)–C(14)	2.029(11)
		Ni(2)–C(25)	1.996(11)
C(9)–C(10)	1.376(8)	C(13)–C(14)	1.363(16)
		C(24)–C(25)	1.381(15)
Ni(1)–O(1)–C(12)	125.8(3)°	Ni(1)–O(3)–C(3)	129.6(7)°
		Ni(2)–O(4)–C(3)	127.3(7)°
Ni(1')–O(2)–C(12)	125.6(3)°	Ni(1)–O(1)–C(1)	130.1(7)°
		Ni(2)–O(2)–C(1)	128.3(7)°

strongly bonded to the nickel ions than the other one. This means that in the two complexes the two acetate groups are differently bonded in the two halves of the dimeric molecules, as indicated by the lengthening of the Ni–Ni distance and the slight increase of the Ni–O–C angles in III with respect to II.

While in I we found evidence for some direct interaction between the two Pd ions[3], such interaction between the smaller Ni ions is questionable for II and very unlikely for III.

The fact that the differences in the experimental conditions necessary to obtain crystals of the two Ni complexes are so small[4], suggest the possibility that the two isomers coexist in solution, and that the exchange between the two forms may depend on the dissociation of the metal–acetate bonds, as indicated by the strong *trans* effect and the impossibility of obtaining III by simple rotation of one of the methylallylnorbornyl ligands about the Ni–Ni axis in II. As in I, in II and III also the C=C bonds are asymmetrically located with respect to the coordination planes, with the bond axes making angles to these planes of about 77° in II and about 76° and 83° in III. This further corroborates with our previous statement[3] that this shift of the coordinated C=C bond from its "normal" position is not due to steric factors but to the asymmetry induced by the substituents into the π^* orbital of the vinyl ligand.

We plan to discuss these structures further in a later paper when the refinement of the analysis of III and the structural analysis of two other related nickel complexes are finished.

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REFERENCES

1 M. Zocchi, G. Tieghi and A. Albinati, *J. Organometal. Chem.*, 33 (1971) C47.
2 M.C. Gallazzi, T.L. Hanlon, G. Vitulli and L. Porri, *J. Organometal. Chem.*, 33 (1971) C45.
3 M. Zocchi, G. Tieghi and A. Albinati, *J. Chem. Soc., Dalton Trans.*, (1973) 883.
4 M.C. Gallazzi, private communication.